

Pressure dependence of two-level systems in disordered atomic chain

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The dependence of two-level systems in disordered atomic chain on pressure, both positive and negative was studied numerically. The disorder was produced through the use of interatomic pair potentials having more than one energy minimum. It was found that there exists a correlation between the energy separation of the minima of two-level systems Δ and the variation of this separation with pressure. The correlation may have either positive or negative sign, implying that the asymmetry of two-level systems may in average increase or decrease with pressure depending on the interplay of different interactions between atoms in disordered state. The values of Δ depend on the sign of pressure.

PACS numbers: 45.05.+x, 61.43.-j, 62.50.-p

Keywords: Disordered solids; Discrete systems; High-pressure effects

I. INTRODUCTION

As it was ascertained in last years a number of anomalous properties of glasses at low temperatures can be explained supposing that there exist anomalous low-energy excitations: two-level (tunneling) systems (TLSs) [1, 2] and quasi-localized modes [3–5]. A characteristic property of these excitations is their remarkable sensitivity to different impacts including external pressure P .

The pressure dependence of TLSs in glasses, on the basis of rather general arguments, was considered by Phillips [6]. He concluded that the anomalous (negative) value of the Grüneisen constant for vitreous silica may be explained supposing that the TLSs, when pressure is applied, have a slight tendency to become less asymmetric. Such a tendency means that the energy difference between the two potential energy minima of a TLS Δ and the derivative of Δ with respect to P are to some extent correlated, so that the mean value $\langle \Delta \partial \Delta / \partial P \rangle$ differs from zero (and is negative).

In [7], it was shown that the temperature cycling effect on the width of spectral holes, burned in a dye-doped polymer glass at high pressure and low temperature can be understood if one assumes that under external pressure the higher minimum in the potential energy of TLSs gains more energy than the lower minimum. This means that in polymer glasses there also exists a correlation between Δ and $\partial \Delta / \partial P$; however, it is of the opposite (i.e. positive) sign, so that TLSs in these glassy materials become more asymmetric with increasing pressure.

Although the existence of correlation between Δ and $\partial \Delta / \partial P$ in amorphous solids is expected, it is of interest to verify this property of disordered state by direct molecular dynamics simulation. For checking this correlation numerically, one must bear in mind that the concentration of TLSs in amorphous state is usually rather low and therefore quite large clusters of atoms should be involved in computations, making them fairly intricate and

time consuming. A relatively simple opportunity here is to compute one-dimensional (1D) disordered system consisting of a reasonably moderate number of atoms.

In this study, we have carried out the computations of a disordered atomic chain. To produce a disordered state, special pair potentials having more than one energy minimum were employed. In this model, already in a single-component case, one gets the states of the chain with interatomic bonds of different length. In our computations we employed the pair potentials of two types: the potential Z1 in Ref. [8] with Friedel oscillations and the Schilling piecewise parabolic double-well potential [9], which has a discontinuity of its first derivative at the barrier separating the minima.

II. DISORDERED CHAIN WITH SMOOTH MULTI-WELL PAIR-POTENTIAL

Let us first discuss a monatomic chain with the pair potential Z1 [8]

$$V(r) = a e^{\alpha r} \cos(2kr) / r^3 + b(\sigma/r)^n + V_0, \quad (1)$$

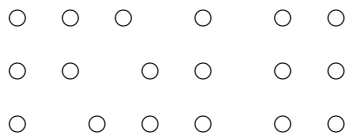
where r is the distance between atoms in proper units. Values of the parameters $a = 1.58$, $\alpha = -0.22$, $b = 4.2 \cdot 10^8$, $\sigma = 0.331$, $n = 18$ are the same as those given in [8] for the potential Z1. The quantity V_0 is a constant (we take $V_0 = 0$). This potential has the sequence of minima and maxima describing the Friedel oscillations. This-type potentials are typical for metals where the oscillations describe the effect of screening of the electric field by free electrons. The parameter k determining the period of oscillations is given by the Fermi wave vector. This parameter will be varied below to show that one can observe distinct kinds of response of the chain to the applied pressure.

In our computations we examined the chain consisting of 400 atoms. We took into account the interactions between 24 nearest atoms (inclusion of more interactions did not noticeably change the results). The disordered state was generated by randomly selecting 20 percent of

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the nearest neighbor pairs of atoms and placing them at the distance, corresponding to the second minimum (situated at $r \approx 1.8$) of the potential given by Eq. (1). All the other nearest neighbor pairs were initially placed at the distance ($r \approx 1.1$), corresponding to the first (main) minimum. The initial configuration of atoms was allowed to relax to the local potential minimum of the chain. In order to find the relaxed configuration, the equations of motion of atoms were integrated using the forth-order Runge-Kutta algorithm. The motion towards the relaxed configuration was accomplished step by step, zeroing of the velocities of all atoms at every five to ten time steps. This procedure was repeated until only negligibly small changes (less than 10^{-8} in our units) in the positions of all atoms were observed, indicating that the final configuration of the chain was reached.

TLSs in the present model are located at the boundaries of "dense" and "rarefied" islands (groups of atoms with small ($r \approx 1.1$) and large ($r \approx 1.8$) distance, respectively). The tunneling transition in a TLS corresponds to the motion of the atom(s) located at the boundary of short and long bonds, resulting in the permutation of two bonds, i.e. in the displacement of a long bond to another position; see, e.g. the changes in the fragment of the atomic chain in the picture below - displacements of atoms (and bonds) cause the transitions between the configurations presented in the different lines of the picture.



A. Free ends

Our first computation was done for the chain with free ends. In the first run, the positions of atoms of the relaxed initial configuration were determined and the potential energy of the chain and its length L_0 were found. After the first run, one of the long bonds was displaced to one of the nearest positions (this displacement corresponds to the single-particle tunneling transition). Then the new coordinates of atoms in the relaxed configuration and the new length were computed and the new potential energy of the chain found. The difference of this energy value from the value corresponding to the initial relaxed configuration gave us the magnitude of Δ . The described runs were repeated with displacements of all other long bonds to the nearest positions, and the values of Δ of all other single-particle TLSs were found.

Our computations revealed that the largest $|\Delta|$ belongs to the TLSs which correspond to the configurations presented in the first and second lines of the picture. If we mark the short bond by 1 and the long bond by 2, then the back and forth tunneling transitions in these TLSs

can be denoted as $(1\ 1\ 2\ 2\ 1) \leftrightarrow (1\ 2\ 1\ 2\ 1)$. The next largest $|\Delta|$ belongs to the TLSs which correspond to the configurations presented in the second and third lines of the picture (the tunneling transition in these TLSs can be denoted as $(1\ 2\ 1\ 2\ 1) \leftrightarrow (2\ 1\ 1\ 2\ 1)$). The configurations with more than two adjacent long bonds, e.g., $(1\ 2\ 2\ 2\ 1)$, $(1\ 2\ 2\ 2\ 2\ 1)$, etc., lead also to the TLSs with a comparable $|\Delta|$. The concentration of these structures in our case is the smaller the larger is the "rarefied" island. In the model under consideration, the structures with extra long bonds corresponding to the third, the fourth, etc. minimum of the potential given by Eq. (1) can also exist. However, these structures were ignored relying on the physical argument of their weak stability.

The energy difference Δ of a TLS depends also on the degree of disorder. This dependence is caused by the interaction of the described above central atoms of the TLS with the surrounding atoms. This conclusion is supported by consideration of the chains with lower and higher concentration of long bonds. Namely, it was found that in the first case the dispersion of the values of Δ of the TLSs with the same configuration of the central atoms is diminished and in the second case enlarged.

We have also studied the cooperative TLSs that correspond to a simultaneous displacement of pairs and larger groups of atoms (e.g. tunneling transitions $(1\ 1\ 2\ 2\ 1\ 1) \leftrightarrow (2\ 1\ 1\ 2\ 1\ 1)$, $(1\ 2\ 1\ 2\ 1\ 2) \leftrightarrow (2\ 1\ 2\ 1\ 2\ 1)$, etc). It was found that the main conclusions which were drawn above for single-particle TLSs, hold also for cooperative TLSs. However, as more particles have to move, the effective mass of the tunneling group of atoms is increased, which implies rather long relaxation times. Therefore, the contribution of such TLSs to low-temperature characteristics can be neglected on a time scale much shorter than the corresponding relaxation time [10].

B. Isobaric and isochoric tunneling transitions

The difference of the lengths of different configurations of the chain with free ends is very small as compared to L_0 . The larger the L_0 is the smaller is the pressure and the work required for bringing the lengths of these configurations to the same length L_0 . Thus, for sufficiently large L_0 , the energies of the configurations of the chain with free ends are practically equal to the energies of the corresponding configurations of the chain with fixed length L_0 . The same is true for the corresponding values of Δ .

An analogous situation exists for isobaric and isochoric tunneling transitions for nonzero pressure. An external pressure applied to the ends of the initial configuration of the chain causes the change of the length of the chain from L_0 to L . In the isobaric case (the pressure P is fixed) after a tunneling transition the latter length in its turn changes from L to $L + dL$. The difference Δ of the energy of corresponding configurations includes the term PdL . The work required to bring these configurations to

the same length L , i.e. to the isochoric case, is also PdL if we assume the change of P required for bringing the lengths of these configurations to the same length L to be negligibly small. The larger the chain is the better this assumption is fulfilled, and the smaller is the difference between the isobaric and isochoric Δ values. In our case of the chain of 400 atoms the difference is less than 0.1 %.

Here, following [6] we consider the isochoric tunneling transitions. We take pressure P in reduced dimensionless units according to the relation $P \equiv (L_0 - L)/L_0$. The case $P = 0$ corresponds to the free ends of the initial (i.e. prior to the tunneling transition) configuration of the chain.

C. Effect of compression

In the next step the effect of positive pressure (in our case a uniaxial compression of the chain) was examined. Here the positions of the end atoms were fixed so that the length of the chain L would be the same (in the $P = 0$ case) or shorter (in $P > 0$ case) than the length L_0 of the initial relaxed configuration of the chain with free ends. The initial positions of all other atoms were chosen so that the distances between atoms would be uniformly reduced. By using this initial condition, the relaxed positions of all by end atoms were computed and the potential energy of the chain found. Then in a similar manner as in the runs without pressure, one of the long bonds was displaced to another (nearest) position, the new relaxed configuration was computed and the new potential energy found. The difference between this energy value and the value corresponding to the initial relaxed configuration gave us the energy difference of the two minima of a TLS at a pressure P , denoted by $\Delta(P)$. The described runs were also repeated with displacements of all other long bonds, and the values of $\Delta(P)$ of all other TLSs were found.

Figures 1 and 2 show the obtained dependence of $\Delta(P) - \Delta(0)$ on $\Delta(0)$ for different TLSs at a small pressure $P = 0.001$ in the case of the potential Z1 given by Eq. (1) with the parameters $k = 4.12$ and $k = 4.5$, respectively. From these figures it is clearly seen that $\Delta(0)$ and $\Delta(P) - \Delta(0)$ are correlated. The sign of the correlation may be different: in the case $k = 4.12$ (Fig. 1) the correlation is positive (TLSs become more asymmetric under pressure), in the case $k = 4.5$ (Fig. 2) it is negative. The correlation is almost complete. However, there exist intermediate cases (with overall weak dependence of Δ on P) where the correlation is insignificant (see, e.g., Fig. 3).

Note further that in the case $k = 4.12$ the minimum of a TLS with a higher energy corresponds to a larger length of the chain with free ends. However in the case $k = 4.5$ the relation between energy and length is just the opposite: the minimum with larger energy corresponds to a smaller length. In both cases the larger is the length,

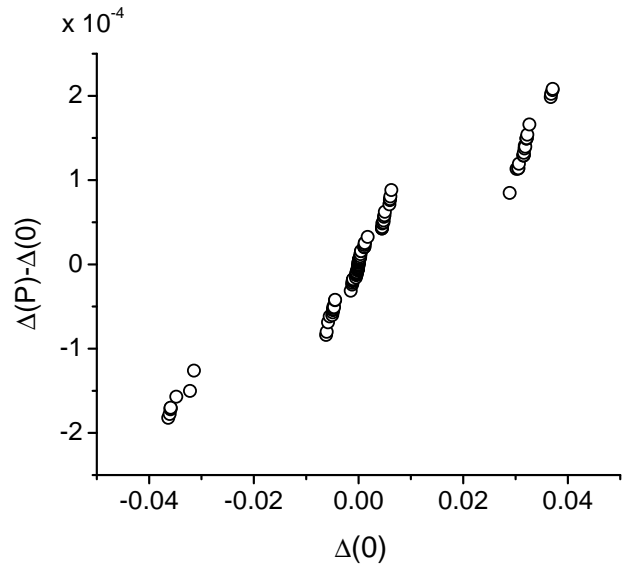


FIG. 1: Changes in Δ of TLSs under dimensionless pressure $P = 0.001$ in the disordered atomic chain with the pair potential Z1. The presented case corresponds to $k = 4.12$ in Eq. (1); the other parameters are given in the text.

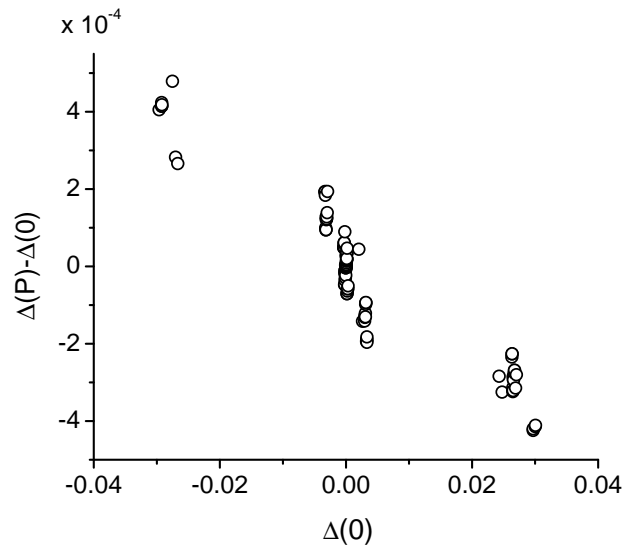


FIG. 2: The same as in Fig. 1, but for $k = 4.5$.

the bigger is the change (increasing) of the energy with pressure. This can be understood as follows - to compress the chain extra energy is needed, which is the larger the larger is compression.

Unlike the case of low P values, in the case of high P values the correlation between Δ and $\partial\Delta/\partial P$ was found to be always positive. In the region of high enough pressures the TLSs are more asymmetric than at zero pressure. It is clearly seen in Fig. 4, where the dependence of the energy differences Δ of two TLSs of the types $(1\ 1\ 2\ 2\ 1) \leftrightarrow (1\ 2\ 1\ 2\ 1)$ and $(1\ 2\ 1\ 2\ 1) \leftrightarrow (2\ 1\ 1\ 2\ 1)$ on

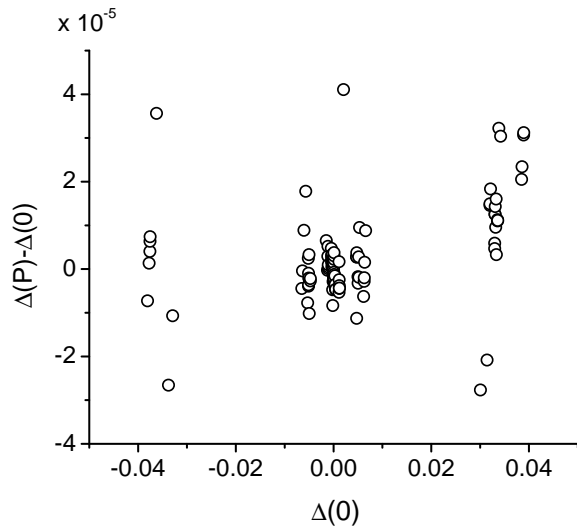


FIG. 3: The same as in Fig. 1, but for $k = 4.3$.

dimensionless pressure P is given for the chain with the same interaction parameters as in Figs. 1 and 2. The upper values of P in Fig. 4 correspond to the critical pressure at which the abrupt changes in a chain begin to occur. Such changes take place when some long bonds transform into the short bonds, which results in disappearance of respective TLSs. Obviously, this happens in such a manner that TLSs gradually increase their asymmetry. With further increase of pressure more and more TLSs disappear. At sufficiently high pressure $P \sim 0.1$ there remain no TLSs at all and the chain becomes ordered.

The presented results are in agreement with the experiments [11–13], where a reduction in the number of TLSs and soft localized modes with pressure in glasses was observed. The reduction in the number of states of a disordered structure with the growth of its density was earlier found theoretically in [14] by an analytical study of a chain of particles with Schilling piecewise parabolic double-well potential [9]. An analogous result was obtained in [15] by the molecular dynamics simulation of 32 and 108 particles with the finite-range Lennard-Jones interaction between them.

D. Effect of stretching

It is reasonable to expect that the response of a glass to the volume contraction and dilatation should be different [16, 17]. If so then the value of $\Delta(P)$ should depend on the sign of P . In order to control this statement we performed computations of TLSs also for negative P (in our case for uniaxial stretching of the chain). We have found that, indeed, the value of the energy Δ of a TLS depends on the sign of pressure, which can clearly be seen in Fig. 4. Only in the case of a large $|P|$ the change of Δ with $|P|$ for positive and negative P is similar:

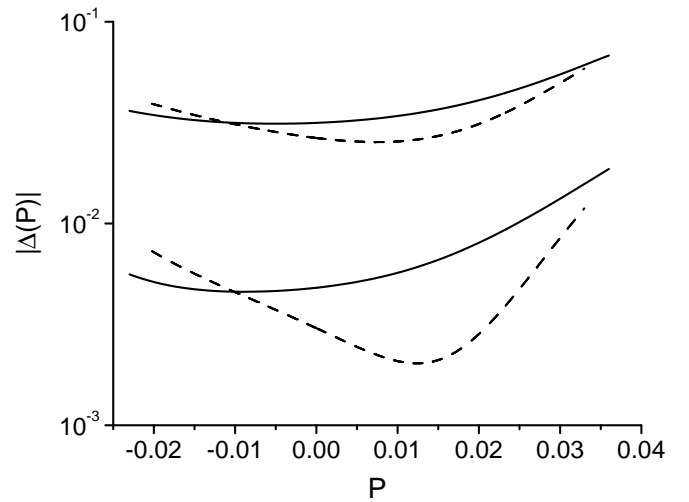


FIG. 4: Pressure dependence of $|\Delta|$ in the disordered atomic chain for the two TLSs with the largest $|\Delta|$ values. Pair potentials are the same as in Figs. 1 and 2; solid lines correspond to $k = 4.12$ while dashed lines to $k = 4.5$.

in both cases Δ increases with $|P|$. It was also found that at negative pressure $P \approx -0.02$ the chain breaks down.

III. DISORDERED CHAIN WITH PIECEWISE PARABOLIC DOUBLE-WELL POTENTIAL

Lastly we have performed computations of the pressure dependence of 1D disordered chain with the Schilling-type piecewise parabolic double-well potential for nearest neighbors [9, 14]

$$V_1(r) = V_0 + a_1(r - r_1)^2 \Theta(r_0 - r) + [a_2(r - r_2)^2 + b] \Theta(r - r_0), \quad (2)$$

where $\Theta(x)$ is the Heaviside step function. In [9, 14] only the case $a_1 = a_2$ was considered. Here the values of parameters $V_0 = -0.743$, $a_1 = 40$, $a_2 = 5.4$, $b = 0.6$, $r_0 = 1.357$, $r_1 = 1.13$, $r_2 = 1.88$ were chosen such that the minima of the potential given by Eq. (2) would coincide with the first two minima of the used above potential Z1. In the model [9, 14], besides the interaction between nearest neighbors, also the interaction with next-nearest neighbors is taken into account. This interaction is represented by a parabolic potential

$$V_2(r) = c(r - r_3)^2. \quad (3)$$

We took $c = 0.05$ or $c = -0.05$ and $r_3 = 4.0$. The results of computations of TLSs for small dimensionless pressure $P = 0.001$ are shown in Fig. 5. It is clearly seen that the quantities $\Delta(0)$ and $\Delta(P) - \Delta(0)$ are correlated, and the correlation is complete and negative. The variance of the TLSs parameters is very small - much smaller than in the case of the potential Z1. This is a consequence of a strong localization of the Schilling interactions.

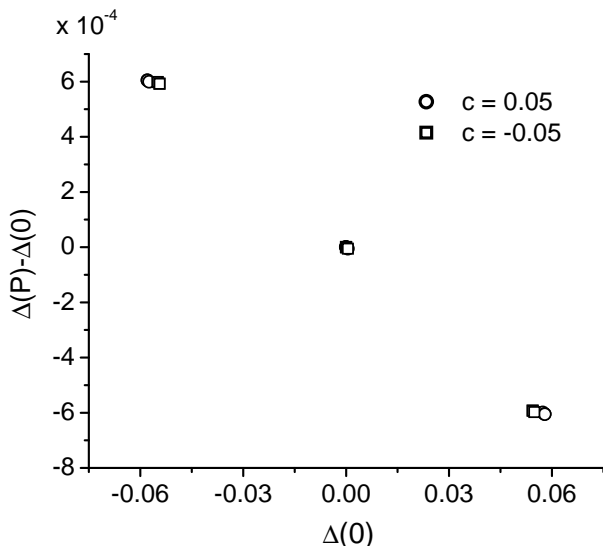


FIG. 5: Changes in Δ under dimensionless pressure $P = 0.001$ in a disordered chain with the Schilling-type pair potential. The presented cases correspond to $c = 0.05$ and $c = -0.05$ in Eq.(3); the other parameters are given in the text.

We have also performed computations for other values of the parameters of the potentials $V_1(r)$ and $V_2(r)$. It appeared that the sign of the difference $a_2 - a_1$ determines

the sign of the correlation between Δ and $\partial\Delta/\partial P$: if $a_1 > a_2$ then the sign of the correlation is negative, thereby if $a_1 < a_2$ then the sign is positive. In the case $a_1 = a_2$ the values of Δ do not depend on P . In the large P limit all the TLSs disappear.

IV. CONCLUSION

Molecular dynamics simulations of 1D disordered state unambiguously testify that for two-level systems there exists a correlation between the magnitudes of Δ and their alterations under external pressure. The correlation may be either positive or negative sign. This signifies that the asymmetry of two-level systems may in average increase or decrease with pressure, depending on the interplay of interactions between particles in the disordered state. The response of TLSs to external pressure depends on the sign of pressure.

V. ACKNOWLEDGEMENT

The research was supported by the Estonian Science Foundation through Grant No. 7741. The authors are grateful to Prof. J. Kikas and Dr. A. Laisaar for valuable discussions.

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